Perchlorate

Presentation Overview

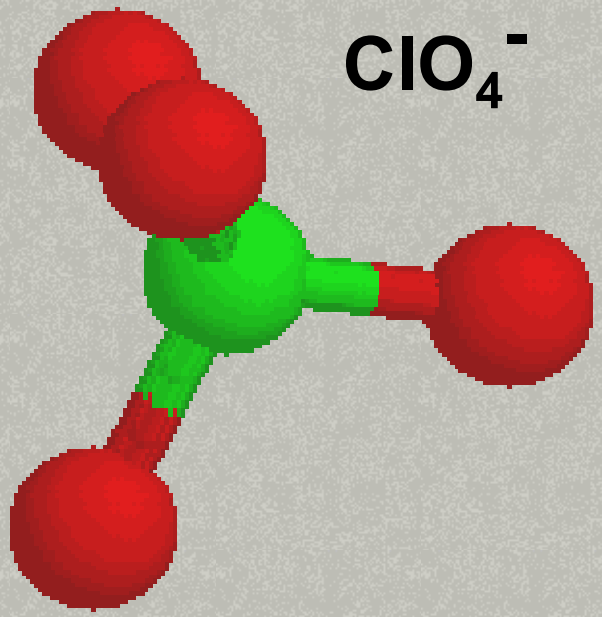
- Background
- Toxicology
- Analytical
- Treatment Technologies
- Case Study
- Work Groups

Background

- Perchlorate (ClO_4^-) chemistry
  - Highly oxidized but generally unreactive
  - It is a salt, in many ways similar to nitrate (NO_3^-)
- What does this mean?
  - Mobile in subsurface but stable: BIG PLUMES!
  - Same for surface water: LARGE AREA AFFECTED.
  - Treatability:
    - Not technically difficult, but development and optimization required
    - Potentially very costly due to volume of water requiring treatment

Understanding the Problem: What is Perchlorate?

- Primary oxidizer in solid rockets
  - Titan, Minuteman, Peacekeeper, Hawk, Polaris, Space Shuttle
- Used in explosives and fireworks
- Found in fertilizers
- Medicine
- Neither sinker nor floater
- Very stable in water



Uses of Perchlorate

Ammonium Perchlorate:

A National Technical Asset Integral to Defense Systems

- Tactical and Strategic Rocket Motors
- Mines
- Torpedoes

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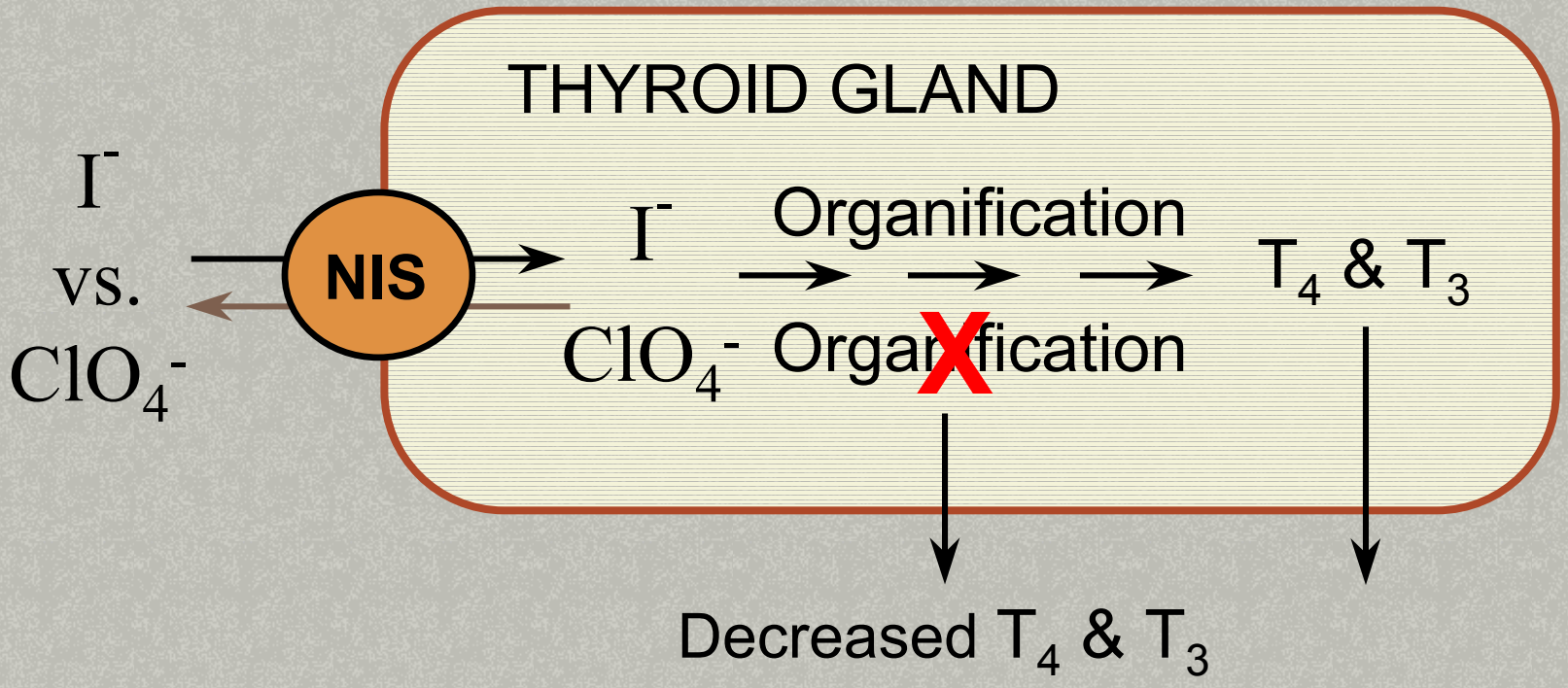
Health Effects

NIS = Sodium Iodide Symporter

T_3 = Triiodothyronine

T_4 = Tetraiodothyronine (Thyroxine)

Perchlorate and the Thyroid Gland



Main Symptoms/ Effects of Hypothyroidism

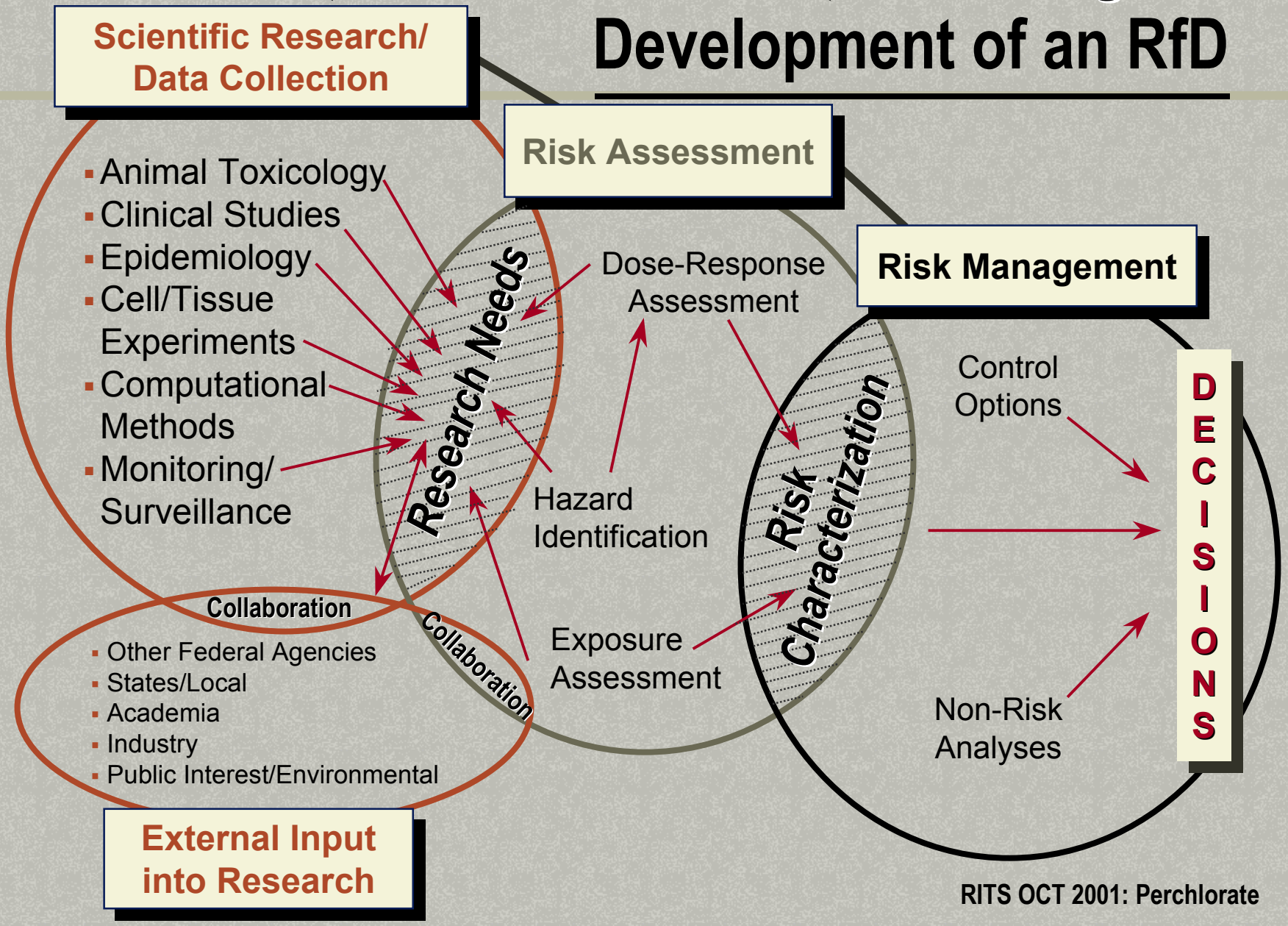
- Adult diagnosed with hypothyroidism usually due to iodine deficiency:
  - Run down, slow, depressed,
  - Sluggish, cold, tired
  - Dryness and brittleness of hair
  - Dry and itchy skin, constipation
  - Muscle cramps
  - Increased menstrual flow
  - Possibly goiter

transient disruption leads to transient effects

Source: National Health and Environmental Effects Laboratory

Research ⇄ Assessment ⇄ Management

Development of an RfD

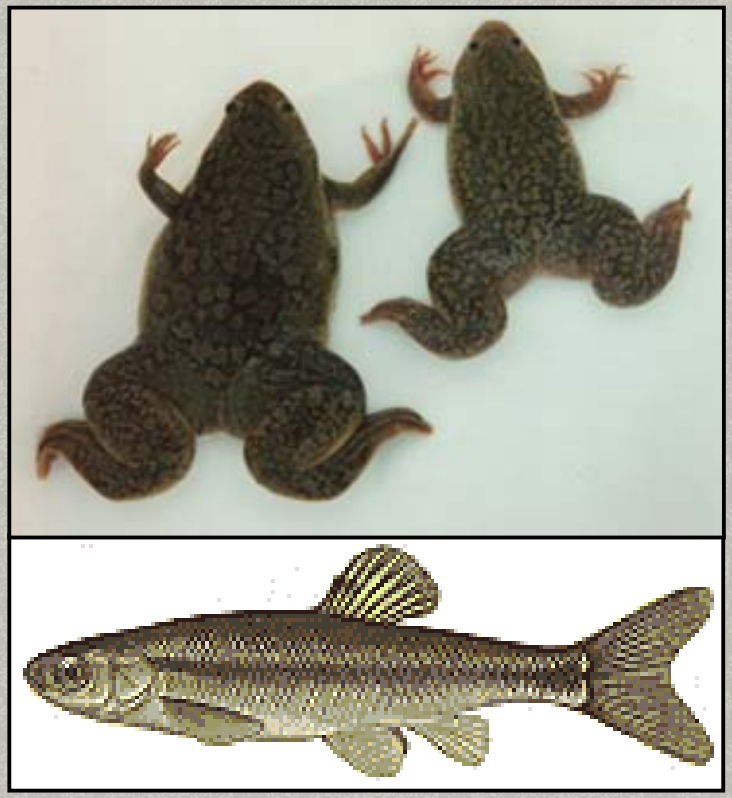


Oral Reference Dose (RfD) Definition

- An RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious noncancer health effects during a lifetime.

Ecological Impacts

- Data gaps identified after external peer review, April 1999
- Performance of toxicity assays
- Biotransport studies
  - Detection
  - Relationship



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Special Considerations and Sample Preparation

- Water (drinking and ground) U.S. EPA Method 314
  - Total dissolved solids (TDS)
- Other Matrices
  - Solids (fertilizer and soil)
  - Serum (rat and human)
  - Urine (rat and human)
  - Tissues (rat)
  - Milk (rat)
- NSWC Indian Head Developments

AS-11 vs. AS-16 Column Studies

AS-11

- Older
- Not as sensitive or selective
- Not as robust
- Better for high TDS samples

AS-16

- Newer
- More sensitive/selective
- More robust
- More compatible w/organic
- Better for biological

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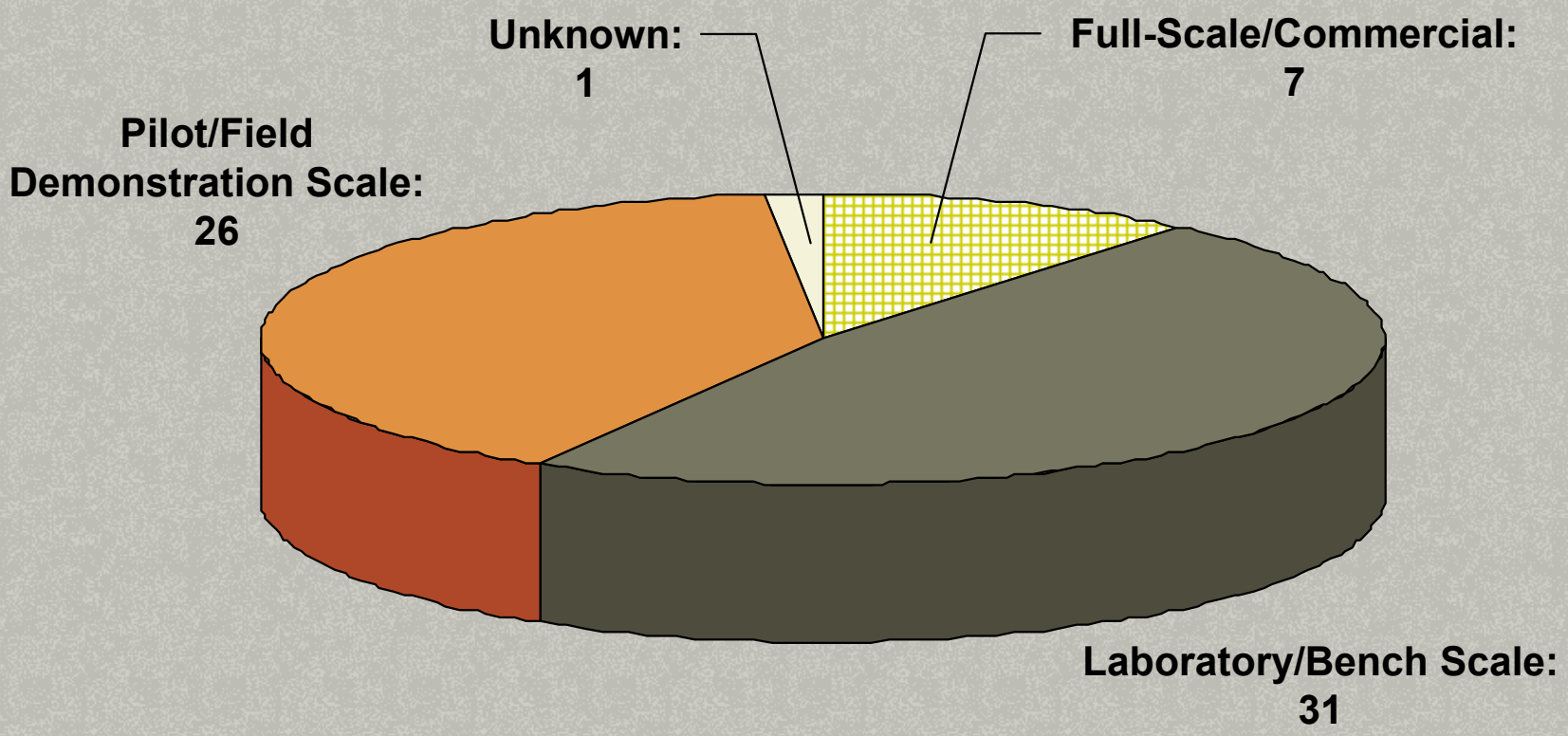
General Categories

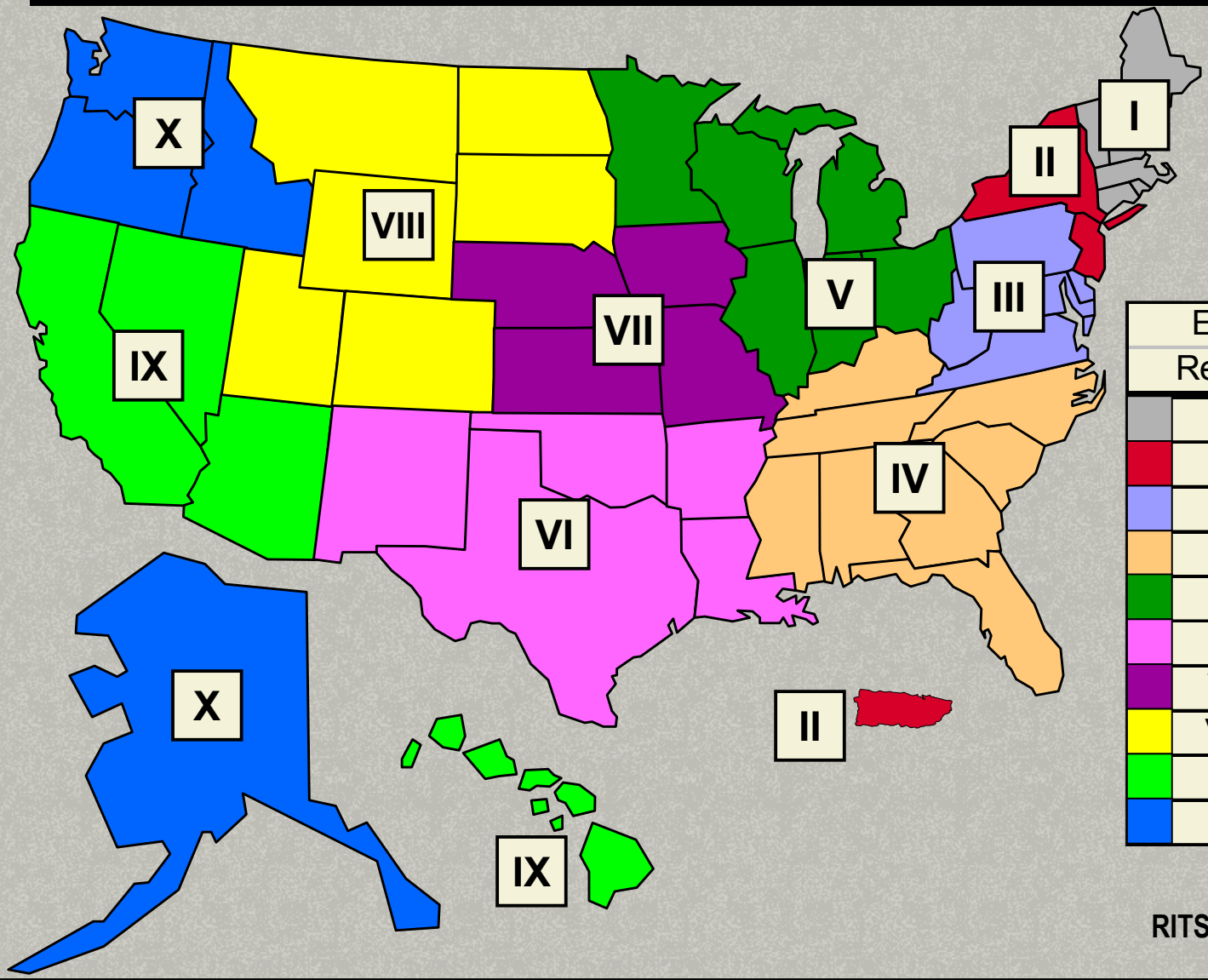
- Physical processes (Ex Situ)
  - Anion exchange
  - Reverse osmosis/nanofiltration
  - Electrodialysis
  - Capacitative deionization
  - Brine treatment and disposal
- Chemical processes (Ex Situ)
  - Reduction (chemical, electrochemical)
  - Oxidation (ozone-peroxide)
  - GAC
  - Catalytic reactor system
- Biological processes (ex situ – anaerobic or anoxic)
  - Biological reduction
  - Biochemical reduction
  - Bioreactors (fluidized bed, packed bed, phytoremediation)
- In situ bioremediation
  - Permeable reactive barrier
  - Substrate injection
- Phytoremediation
  - Pilot pending

Scale of Perchlorate Treatment Technology Projects



Total Number of Projects = 65

Locations of Pilot- to Full-Scale Projects



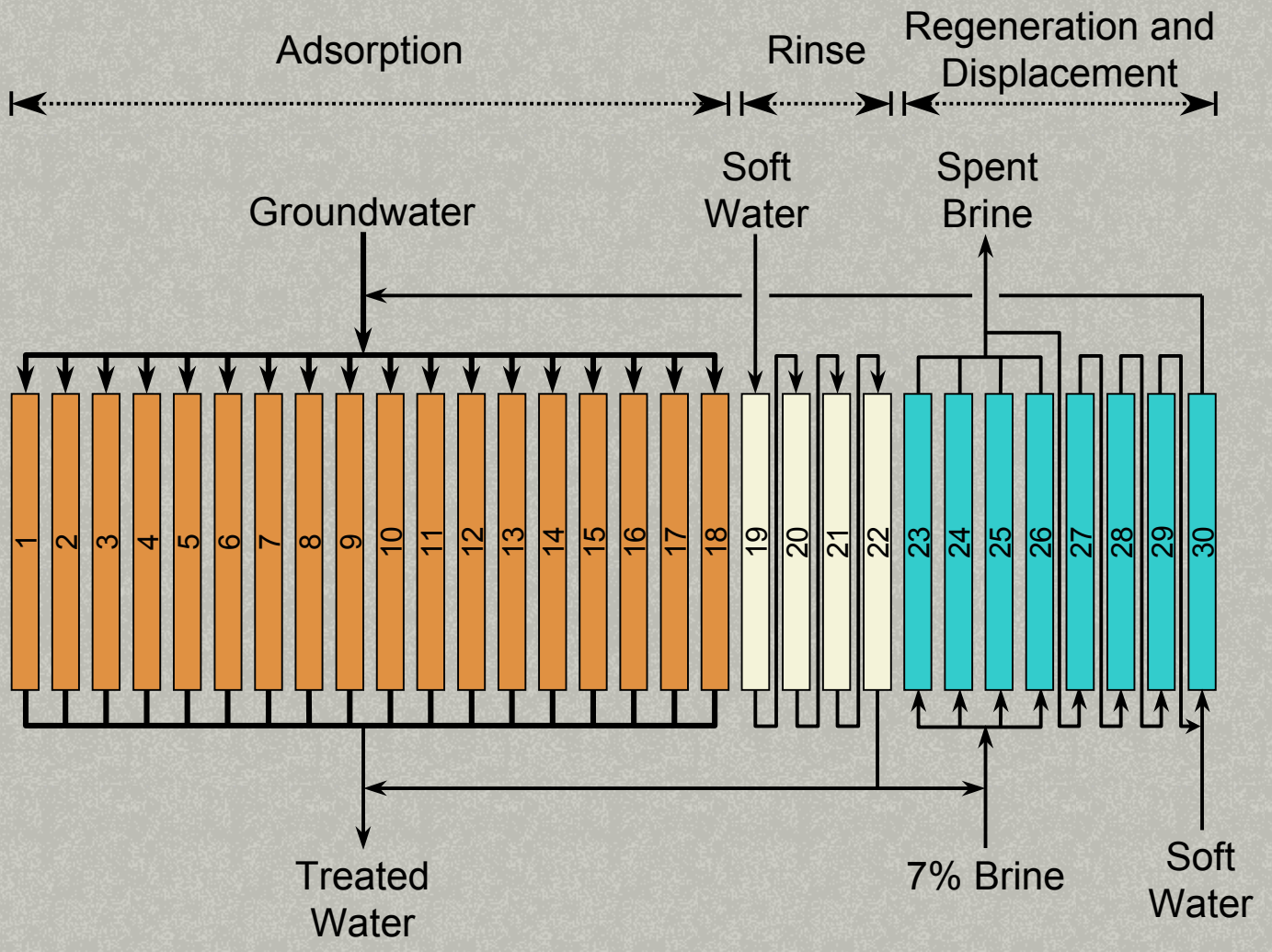
EPA Region	Number of Full/ Pilot Scale
I	0
II	2
III	1
IV	2
V	0
VI	5
VII	0
VIII	2
IX	19
X	0

Perchlorate R&D and Commercial Relationships

- AWWARF (Mgmt. Funding)
  - Northwestern University
  - Penn State University (CDM/ UNLV/City of Redlands, CA)
  - Clarkson University
  - University of Illinois/Metro Water District of S. Calif. (LA)
  - University of Colorado/Nat. Institute of Standards and Technology/ Metro Water District of S. Calif. (LA)
  - University of Houston
- SERDP/ESTCP (Funding)
  - Southern Illinois University
  - Envirogen
  - Geosyntec
- National Science Foundation
  - Penn State University
  - Louisiana State University/ Swiss Fed. Institute of Technology
  - Iowa State University
- San Gabriel Basin Initiative

Ion Exchange Removal of Perchlorate in Groundwater

Process Flow Diagram for ISEP® System, Calgon Corp.



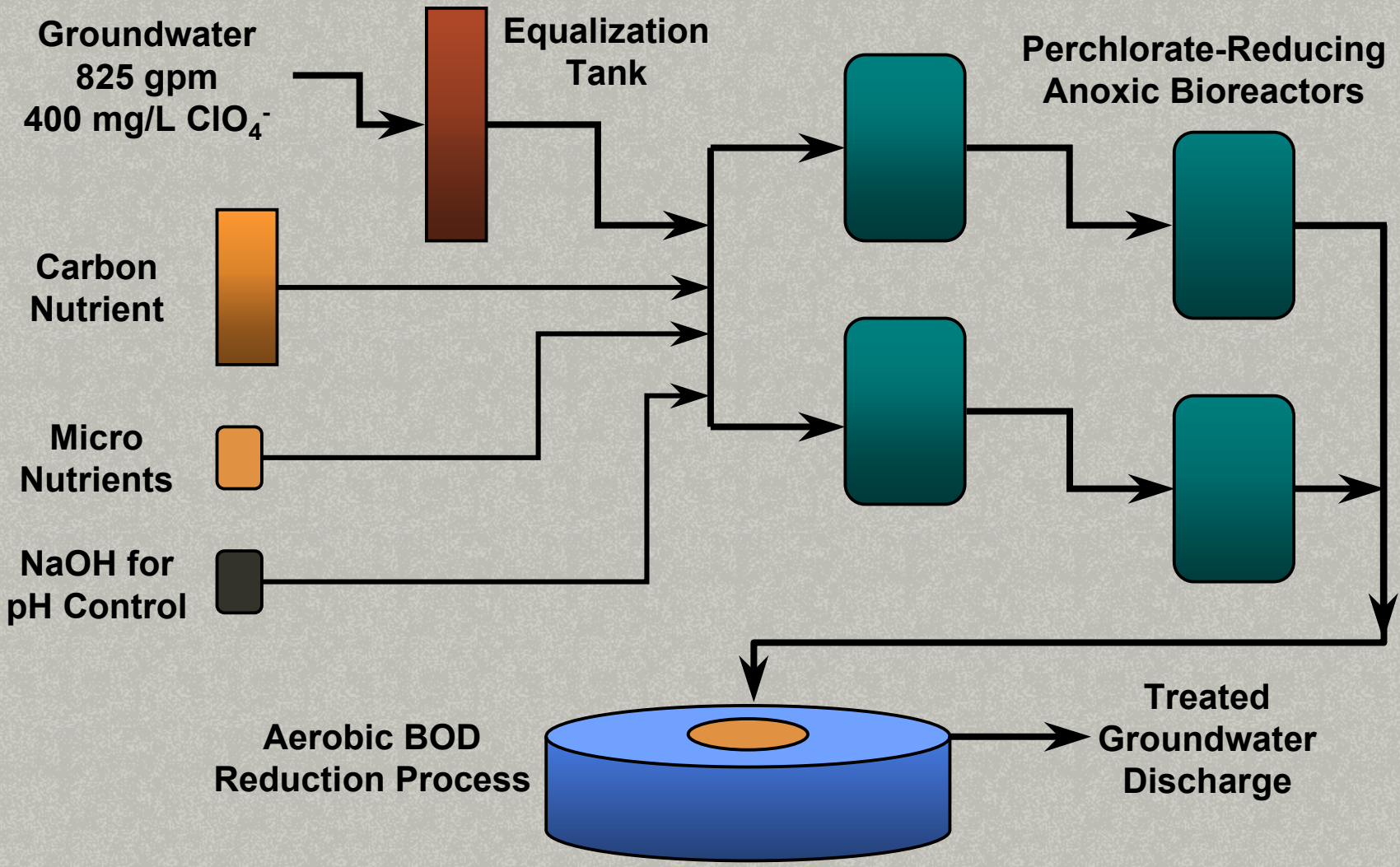
Treatment Technologies

Ion Exchange Removal of Perchlorate in Groundwater

Calgon Corp., La Puente, CA

Biodegradation of Perchlorate in Groundwater

Process Flow Diagram for Kerr-McGee Chemical LLC, Henderson, NV
Applied Research Associates, Inc., Biothane Corporation, Smith & Loveless, Inc.



Biodegradation of Perchlorate in Groundwater

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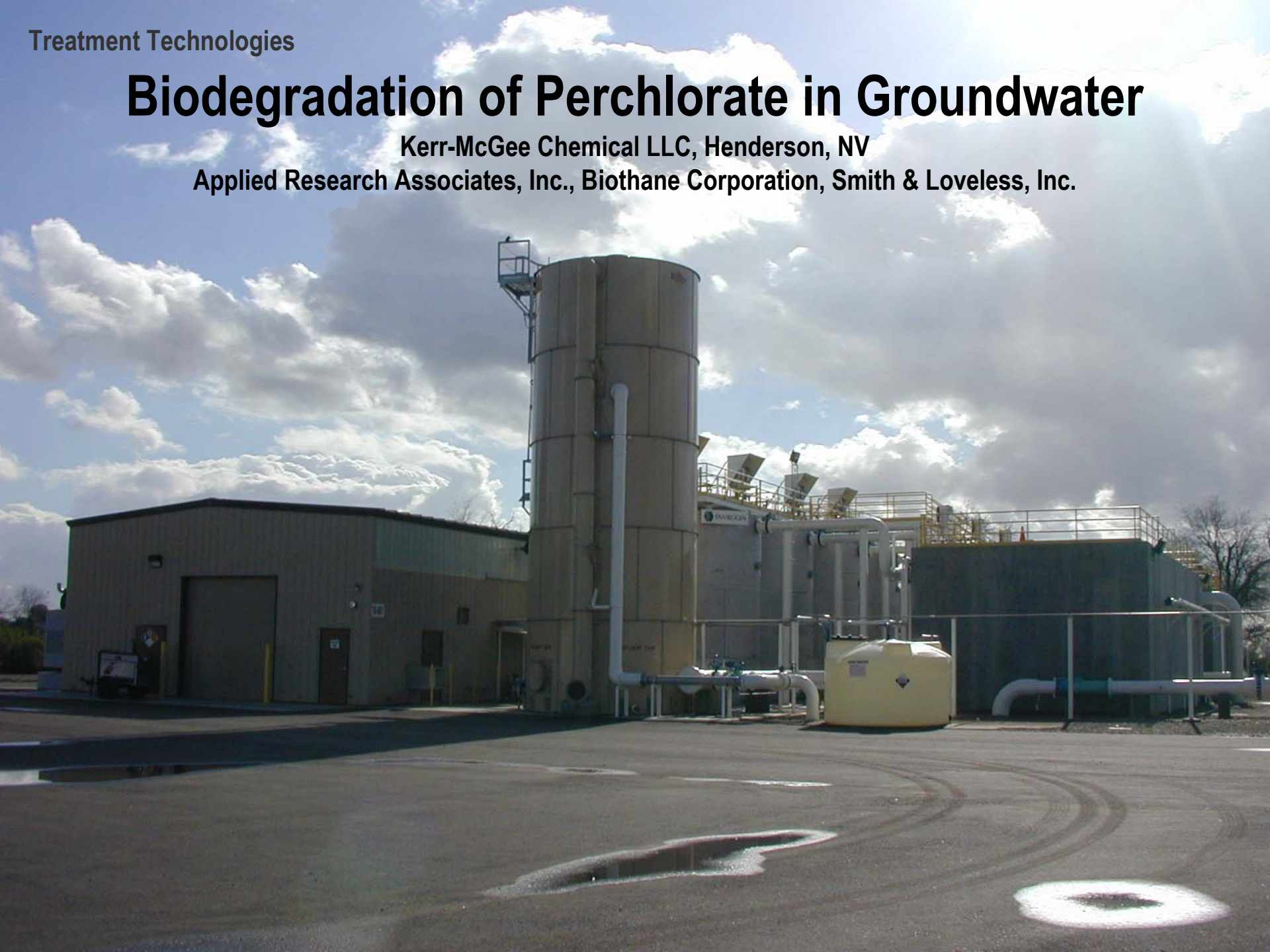
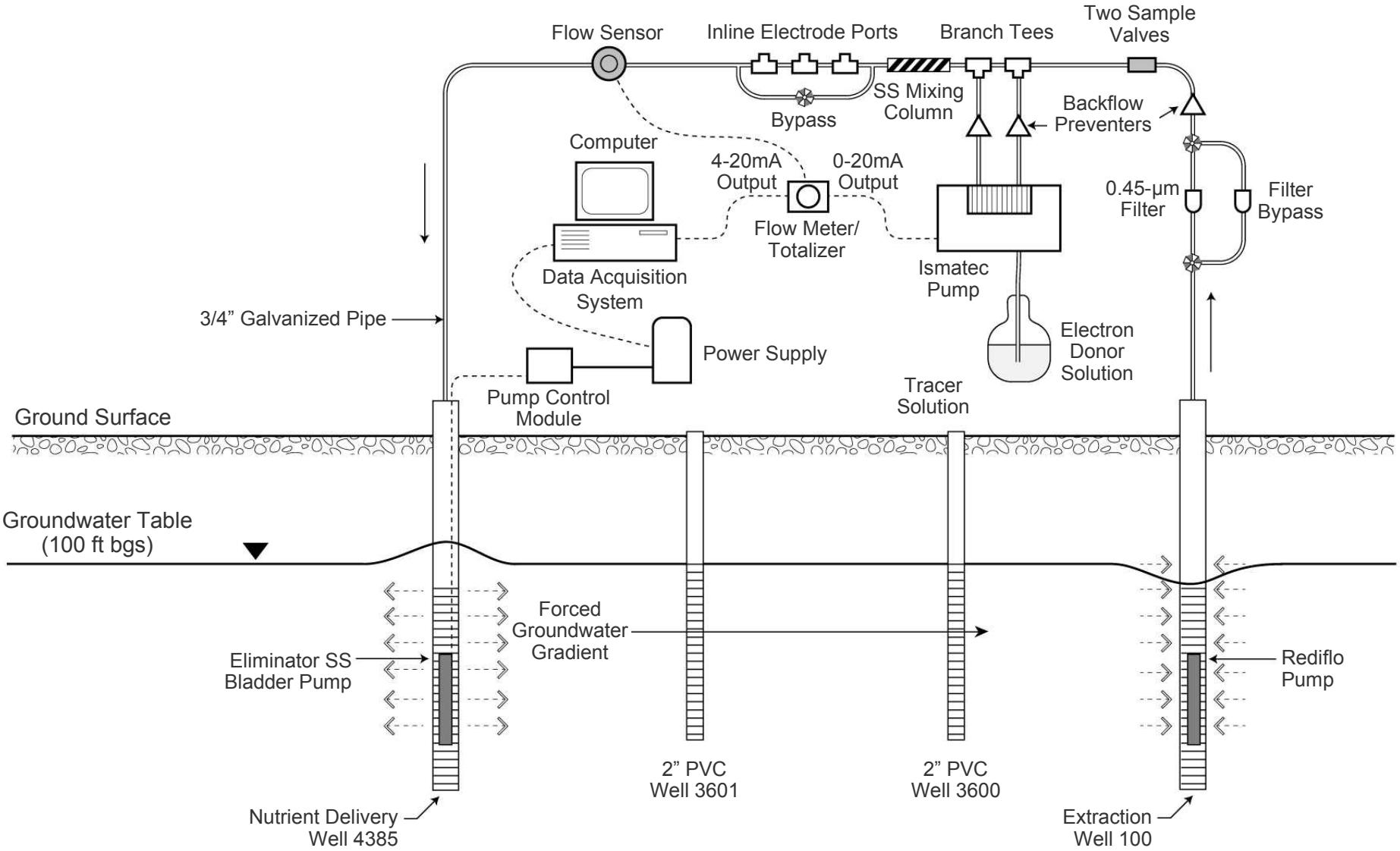


Treatment Technologies

In Situ Bioremediation

Geosyntec Consultants, Aerojet, CA



Flow Rate = 5 gpm

Cross Section Schematic
Area 20 Groundwater Pilot

SERDP/ESTCP

Overview of SERDP bioremediation projects (SIU, Envirogen, and Geosyntec)

- Perchlorate-degrading microorganisms are ubiquitous
  - Samples were collected from around the country
- Site-specific electron donor
- Microcosms degraded perchlorate <30 days
- pH lower than 6 may be a problem
- Field tests just beginning

Overall Status

Overview of all projects

- Biological and physico-chemical technologies
- *Ex situ and in situ*
- All concentration ranges
- Water treatment emphasized, not much attention to soil

Status (cont.)

Chemical Treatment (e.g., Ti(III), Fe^0-UV, H_2O_2/O_3):

- Not mature technology
- Costly
- But more research could prove fruitful

Status (cont.)

Physical Treatment (e.g., ion exchange, membranes):

- Mature technologies, applicable for drinking water
- High capital and O&M costs;
- Looking for ways to optimize these processes

Status (cont.)

Biological Treatment
(e.g., bioreactors, in situ bioremediation):

- Mature technologies,
- Varied cost scenarios
- Need more data to understand bioprocesses
- Much accomplished, many more opportunities….

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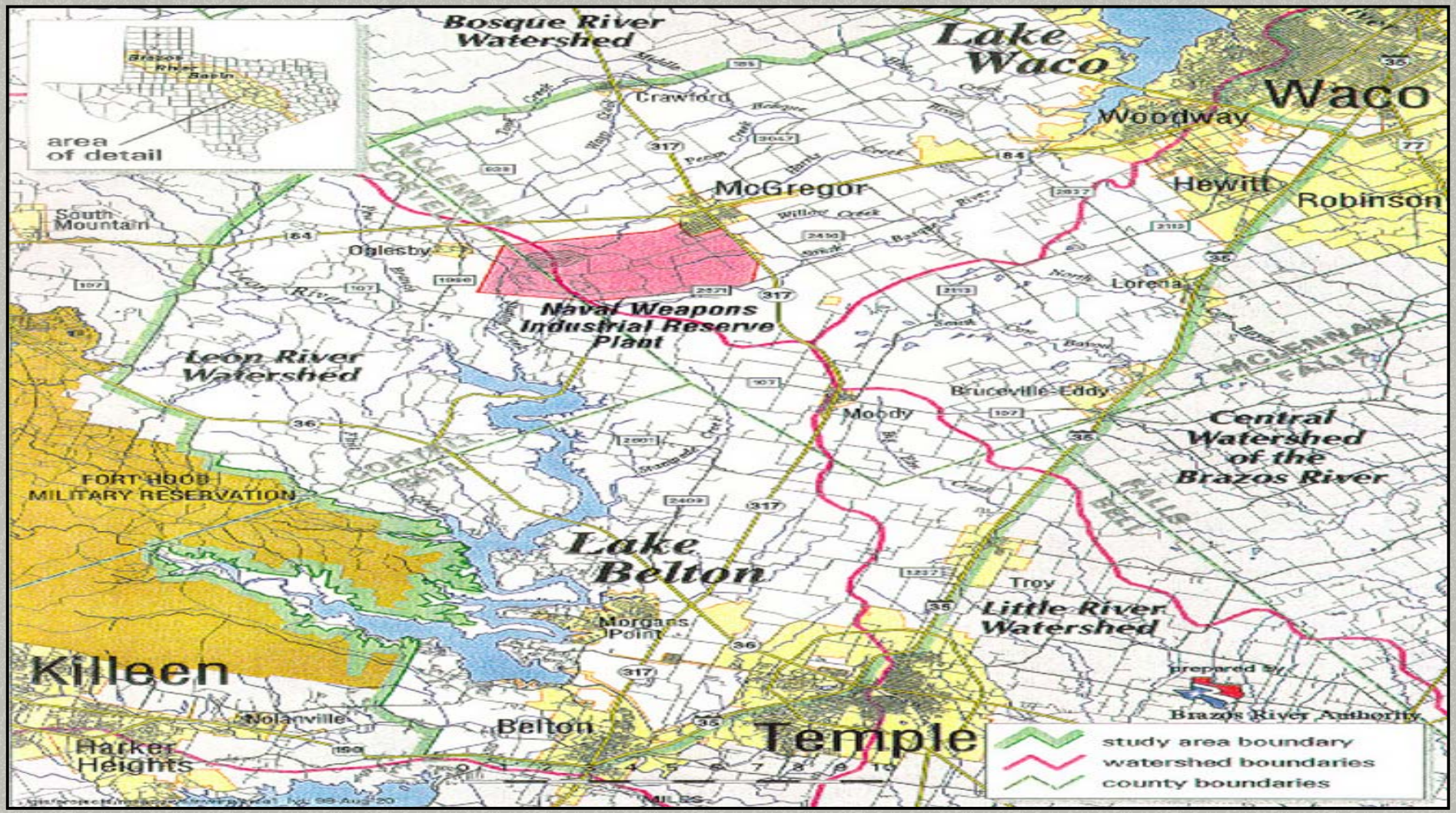
- Work Groups

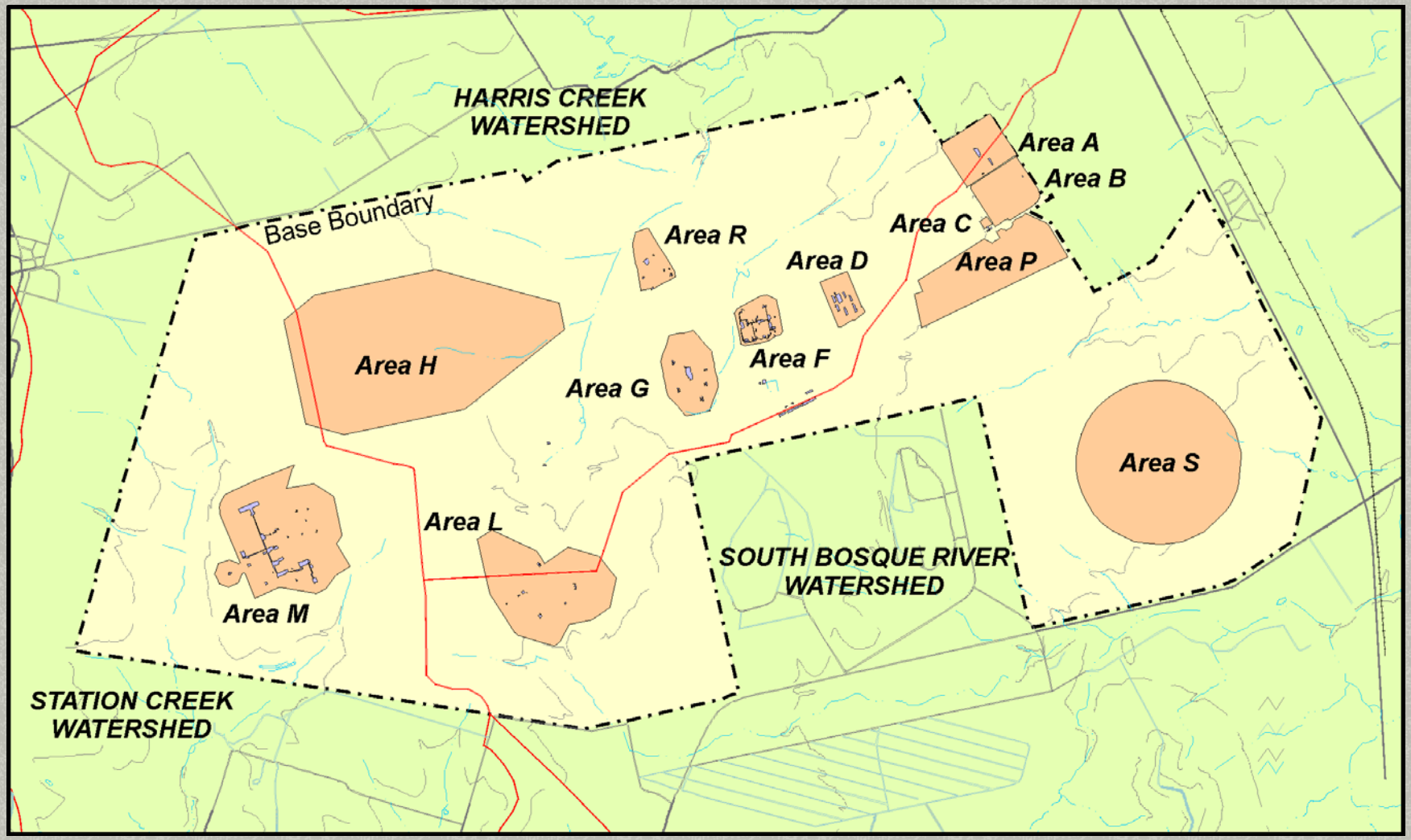
NWIRP McGregor Perchlorate



Site History

- Operated for more than 50 years under various owners and tenants
  - **United States Army, Navy, and Air Force**
- Industrial activities:
  - **Weapons and weapons systems**
    - Bombs, missiles, and explosives
  - Solid-fuel rocket propulsion systems
    - Ammonium perchlorate

Site History (cont.)



Site History (cont.)

- Ongoing RCRA facility investigation
  - **Soil, surface water, and groundwater**
- Gray area investigation
  - **Based on environmental baseline study results**
- Groundwater investigation

Perchlorate Characterization

- Physical properties
  - Volatility
  - Solubility
  - Stability
  - Reactivity
  - Biodegradability
- Electron acceptor
  - Reactive in presence of reducing agent

Perchlorate Characterization (cont.)

Texas regulatory issues/limits

- Drinking and surface water: 22 ppb
  - Texas Risk Reduction Program (TRRP)
- Soil (protective of groundwater): 270 ppb
  - TRRP: Tier I commercial/industrial soil protective concentration limits (PCLs)
- Groundwater: 66 ppb
  - TRRP: commercial/industrial standards groundwater PCLs

Areas of Environmental Concern

Area M: 750-acre watershed

- Onsite perchlorate concentrations
  - Surface water at property line: 5,600 ppb
  - Groundwater: 4 to 91,000 ppb
  - Springs: 22,000 ppb
- Drainage pathway
  - Onsite discharge to unnamed tributary
  - Station Creek
  - Leon River/Lake Belton
  - Drinking water intake

Interim Stabilization Measures (ISMs)

- Why ISMs?
  - Migration of perchlorate-contaminated groundwater and surface water from site
  - Action letter from the TNRCC (February 1999) requiring migration abatement
- Treatment technology evaluation
- Bench-scale studies
- Pilot-scale studies

Bench-Scale In Situ Study

Objective: Evaluate in situ treatment of perchlorate-contaminated groundwater

- Permeable reactive barrier (PRB)
- PRB media evaluation
- Experimental approach
  - Plastic bioreactors (same as groundwater)
  - Influent concentration: 5,000 to 8,000 ppb
  - Flowrates similar to groundwater

Bench-Scale In Situ Study (cont.)

Compost | Oil-Coated Wood Shavings | Cotton Seed | GAC

ISM Selected Strategies

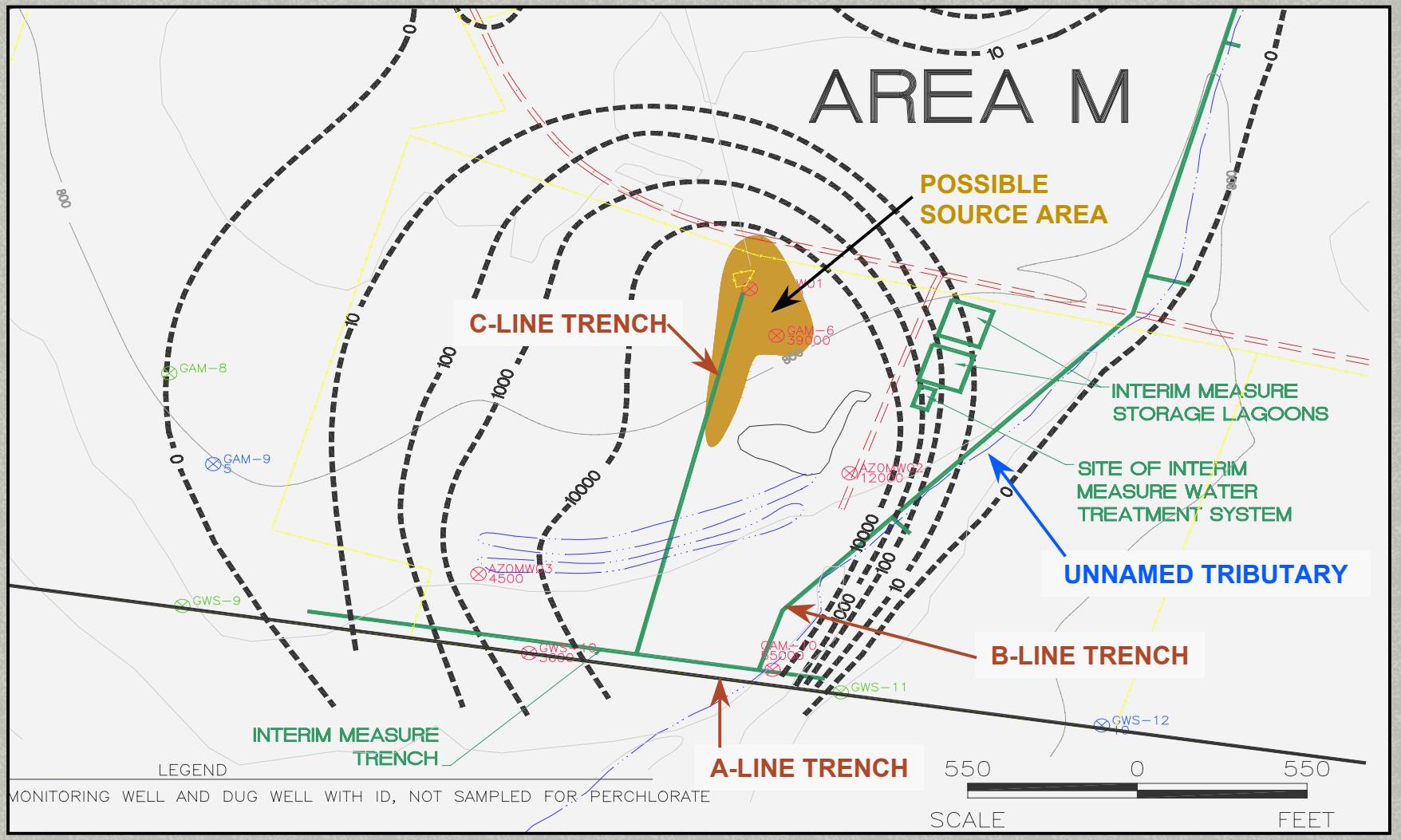
- Groundwater cutoff and collection trenches
- In situ groundwater biotreatment
- Soil biotreatment

Cutoff/Collection Trench Construction

ISM design goals

- Abate off-site migration of perchlorate-contaminated groundwater and surface water
- Interception and collection in trenches
- In situ bioremediation

Cutoff/Collection Trench Construction



Cutoff/Collection Trench Construction

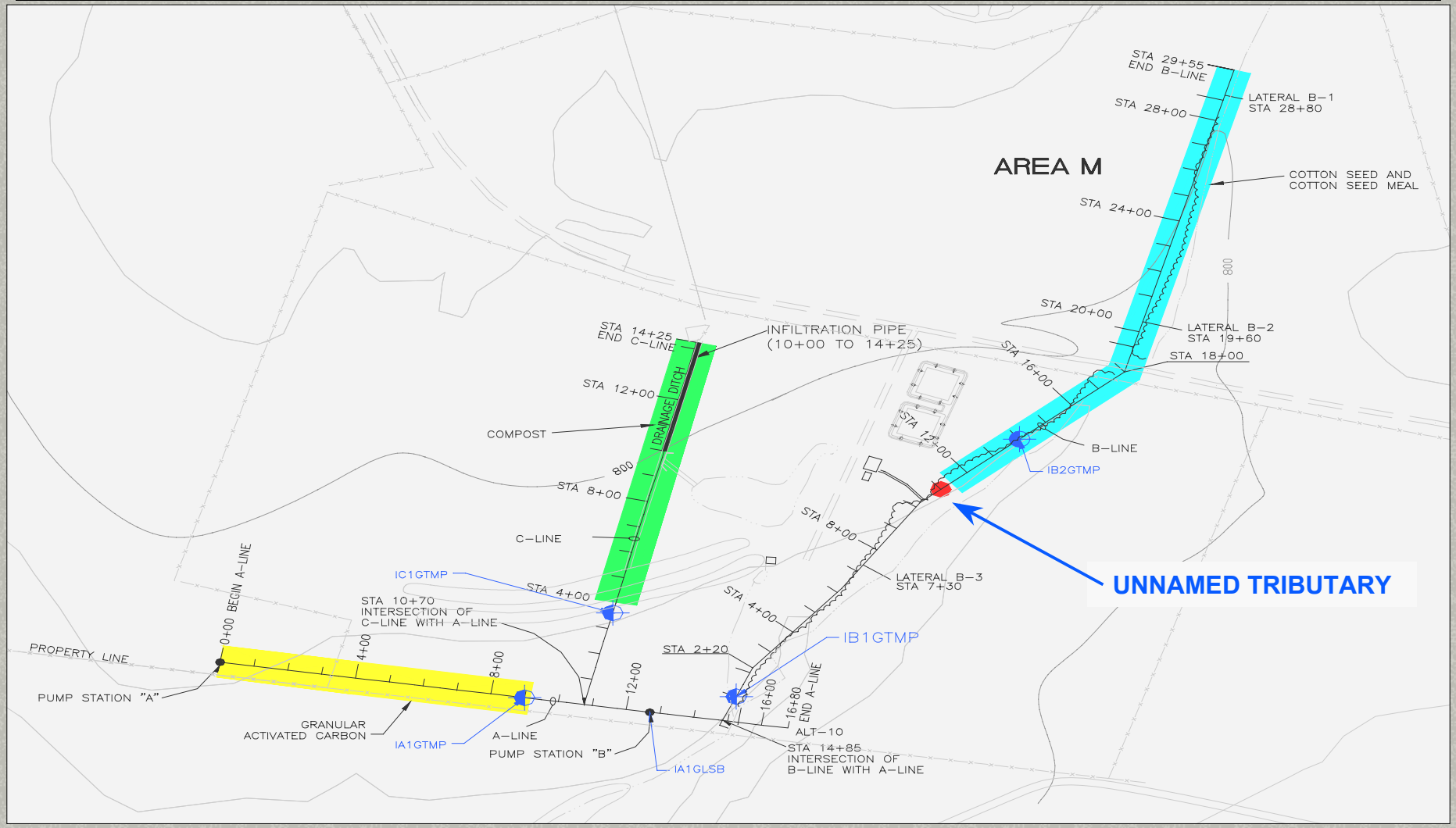
A-Line property line cutoff trench

- Extends through weathered limestone water-bearing zone
- 30 inches wide
- Up to 25 feet deep
- Perforated collection pipe
- Drainage aggregate

Cutoff/Collection Trench Construction (cont.)

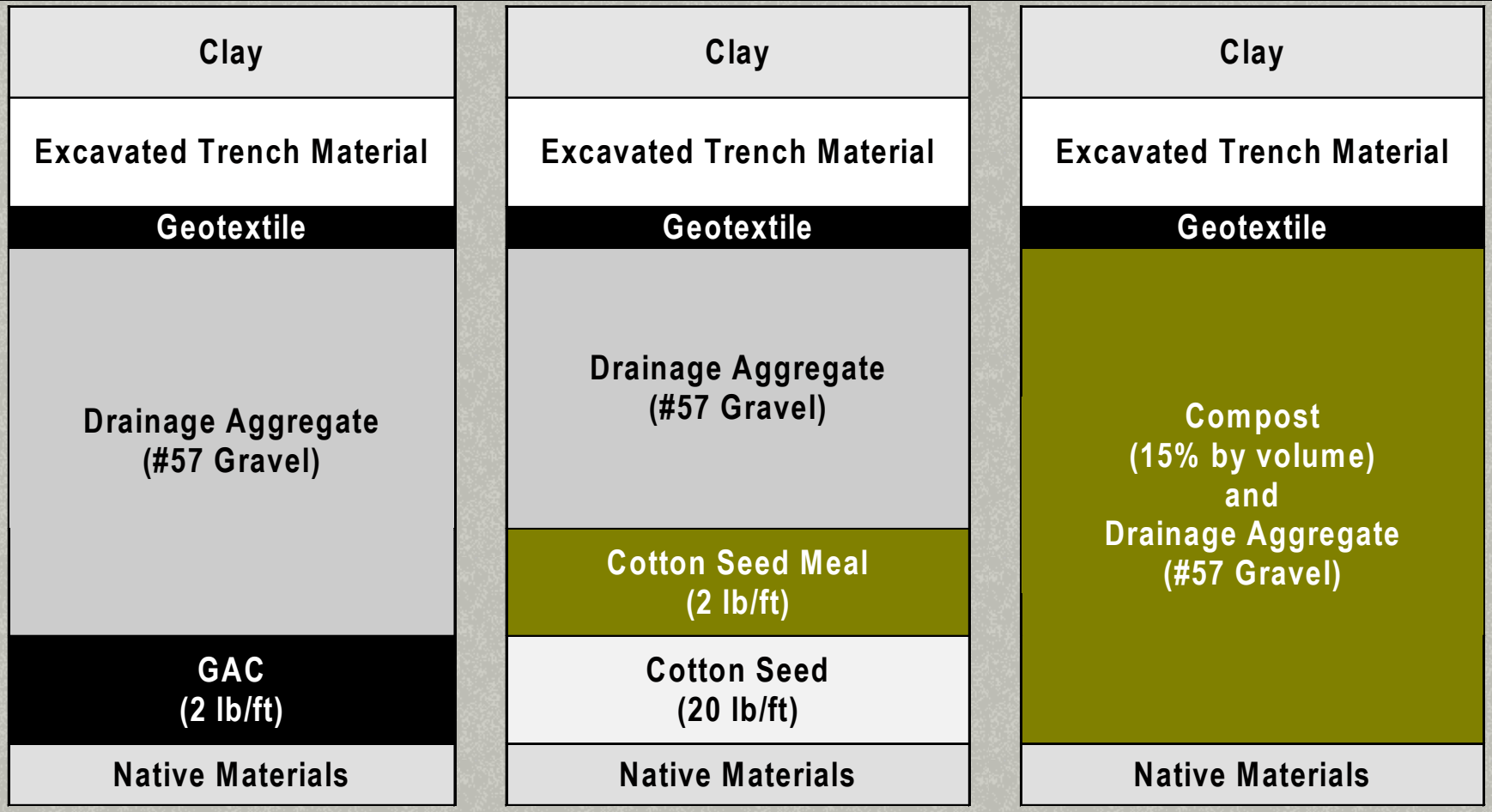
Cutoff/Collection Trench Construction (cont.)

Collection System Modification



Collection System Modification

Collection System



Soil Treatment System

Additional ISM Issues

- Emergency order
  - Originally no discharge allowed
  - Allowed discharged at 22 ppb as of May 2001
  - Should be in effect until TPDES permit is issued
- Winter rains 200% above normal
  - Higher groundwater flow than expected, electron donor amendment
  - 22 million gallons stored during period of no discharge

Site Costs and Cost Savings

- ~$10M for Area M to date
  - Includes site investigations
  - Bench and pilot studies of different treatment systems
  - Full-scale implementation
- Cost avoidance
  - ~$3M in capital costs compared to existing technologies
  - ~$95K per year in O&M

Successes

- Successful partnering initiative
  - **TNRCC and U.S. EPA**
- Fast track implementation
- Seamless relationship between CLEAN and RAC contractors
- Created an avenue to educate and distribute information to the community and stakeholders

Successes (cont.)

- Pilot-scale treatment system used as remedy
- Innovative in situ treatment system rendered ex situ system unnecessary at NWIRP McGregor
  - **Before pilot-scale study**
- ISM cost savings

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  - Inter-Agency Perchlorate Steering Committee (IPSC)
  - DoD Perchlorate Treatment Technology Program

Inter-Agency Perchlorate Steering Committee

- Evaluate and understand potential health risks associated with perchlorate in the environment
- To get the best scientific information on the toxicology of perchlorate for use by the decision makers and most importantly to the public
- Partnering among all stakeholders

Major Partners

- DoD
- NASA
- U.S. EPA
- 14 state regulatory representatives
- Native American tribal representatives
- Perchlorate study group (Industry)
- AWWARF
- USDA, FDA
- Citizen stakeholders

Integrated Approach

- Analytical
- Health effects
- Treatment technology
- Ecological

"Parallel" Development

Stakeholder Forums

- Bring together the experts in health effects/toxicology, ecological impacts/transport and transformation, analytical methods, and treatment technology
- Occurrence information
- Provide information on current initiatives
- Hear public and stakeholder concerns

DoD Perchlorate Treatment Technology Workgroup

- Provide a consistent and coordinated approach to treatment technology development and deployment (TTDD)
- Develop and advocate a vision of success for TTDD efforts
- Develop coordinated DoD representation to:
  - Interagency Perchlorate Steering Committee (IPSC)
  - Interstate Technology and Regulatory Cooperation (ITRC)
  - Federal Remediation Technologies Roundtable (FRTR)
  - Others as appropriate

DoD Perchlorate Treatment Technology Workgroup (cont.)

- Keep ESOHPB updated on technology status
- Serve as information clearing house for DoD and IPSC
- Services: USA, USN, USAF (and their respective service centers)
- Other components: DLA, CoE
- DUSD(ES)
- SERDP/ESTCP

Navy Involvement

- USAF Designated as DoD Lead Agency for Perchlorate
  - Coordinate Perchlorate Efforts
  - Recommend Policy
- Navy has representatives on the Work Groups
- Engineering Field Divisions and NSWC Indian Head have experience with perchlorate

Status

Last count: 65 major treatment technology projects

- 31 lab/bench, 26 pilot, 7 full-scale
- Full-scale:
  - Fluidized bed bioreactors
  - Ion exchange
  - Anaerobic treatment cell (soil)
  - In situ biobarrier (groundwater)
- Numerous university research projects

Looking to the Future….

- Fall 01:
  - IPSC peer review of toxicology studies released to stakeholders and public
  - ESTCP projects start
- FY02: Cleanup standards promulgated by states
- FY03: MCL??

References

Web Sites

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